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Supporting Information

Reversible Photochemical Control of Singlet Oxygen Generation Using Diarylethene Photochromic Switches

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General remarks:

UVASOL grade solvents were used for spectroscopic measurements. UV/vis absorption spectra were recorded on a Specord S 600 (Analytic Jena) spectrometer. UV/vis emission spectra were measured on a JASCO FP-6200 spectrofluorimeter. To avoid interfilter effects, a 3 × 3 mm cuvette was used for the measurements, or otherwise a 1 × 1 cm cuvette. Near-infrared emission spectra were recorded using an Andor iDus InGaAs detector coupled with a Shamrock 163 spectrograph with excitation using a 4 mW 405 nm diode laser (Thorlabs LDM 405). Irradiation at 312 nm was carried out using a spectroline lamp, and visible irradiation using a high intensity fiber optic white light source combined with a 470 nm long pass filter. In general, the PSS can be

reached within 10 s upon irradiation with UV light and the recovery of the open form within 1 min of irradiation with visible light.

Transient absorption spectroscopy:

Triplet absorption lifetimes were determined using a home built system. Excitation was performed using the second harmonic (532 nm, 1-3 mJ, 6 ns) or the third harmonic (355 nm, 1-3 mJ, 6 ns) of a Q-switched Nd:YAG laser (Innolas 400) with a Si-diode trigger sensor. The probe light was from a pulsed Xenon light source (Applied Photophysics). The change in absorbance of the sample was measured using a Zolix Omni- λ 300 monochromator coupled with a 5-stage photomultiplier tube (Gilden Photonics). The decay traces were recorded with a 1 k Ω termination on a Tektronix DPO 4032 digital Oscilloscope.

Solutions of ZnTPP and ZnTPP in the presence of the closed form of **1** were excited at 355 nm, which did not switch the closed form to the open form during the measurement. ZnTPP in the presence of the open form of **1** was excited at 532 nm at relatively high concentration because of the lower molar absorptivity of ZnTPP at 532 nm compared with that at 355 nm. All samples were prepared by at least three freeze-pump-thaw cycles and kept under an argon atmosphere.

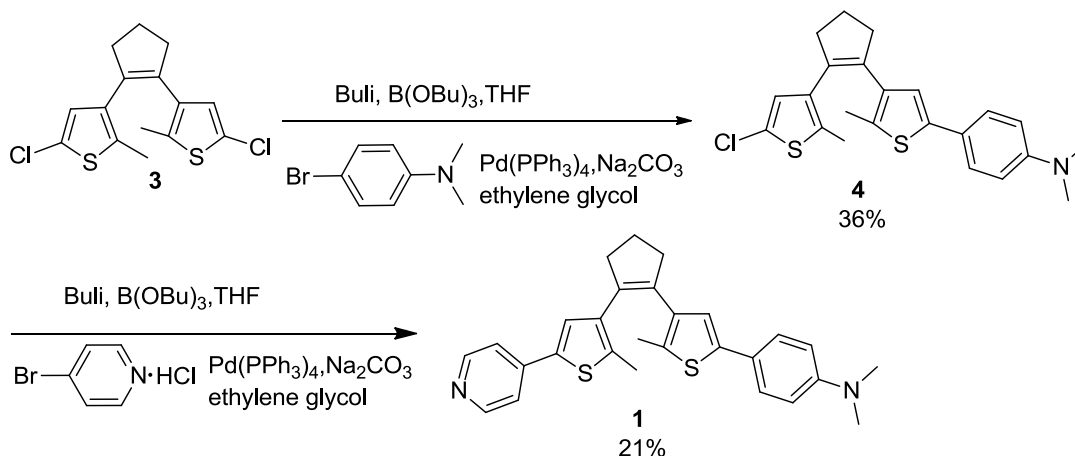
Computational details

Geometries of open **1**, closed **1**, open **2**, and closed **2** were optimized with DFT, using the B3LYP hybrid functional¹ and a 6-31G(d) basis set.² The energy of the T₁ state was then calculated by a single-point energy calculation at the B3LYP/6-31G(d) using an unrestricted wavefunction, after which subtraction of the S₀ energy from the T₁ energy provided the S₀-T₁ energy gap. The S₀-S₁ energy difference was calculated using time-dependent DFT, using the CAM-B3LYP functional³ and a 6-31+G(d,p) basis set. All calculations assumed a free molecule in the gas-phase and were performed with Gaussian 09 revision C.01.⁴

Synthesis

meso-Tetraphenylporphyrin (TPP) and ZnTPP were synthesized according to literature procedures.^{5,6}

Synthesis of switch 1



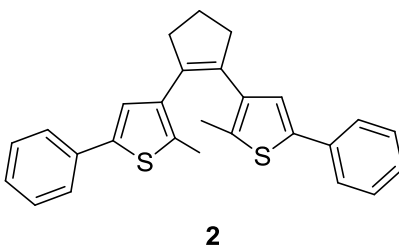
1,2-Bis(5'-chloro-2'-methylthien-3'-yl)cyclopentene¹ **3** (1.003 g, 3.046 mmol) was dissolved in anhydrous THF (40 ml) under a nitrogen atmosphere, and *n*-BuLi (1.6 M in hexane, 3.198 mmol) was added dropwise. The solution was stirred at room temperature for 1 h and then B(*n*-OBu)₃ (3.503 mmol) was added. The reddish solution was stirred for an additional 1 h at room temperature and was then used directly in a Suzuki cross-coupling reaction.

In parallel, 4-bromo-*N,N*-dimethylaniline (691.1 mg, 3.35 mmol), Pd(PPh₃)₄ (703.9 mg, 0.609 mmol), aqueous Na₂CO₃ (2 M, 16 ml) and ethylene glycol (0.4 ml) in THF (24 ml) were heated to 70 °C. The crude boronic ester, prepared as described above, was added and the mixture was heated at reflux overnight. Subsequently, the mixture was diluted with diethyl ether and H₂O. The organic layer was dried over Na₂SO₄, concentrated *in vacuo* and subjected to column chromatography (SiO₂, 30% DCM in pentane) to give a solid **4** (454 mg, 36%). ¹H NMR (400 MHz, CD₂Cl₂) δ 1.89 (s, 3H), 1.95 (s, 3H), 1.99–2.06 (m, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.93 (s, 6H), 6.62 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 14.0, 14.1, 23.0, 38.4, 38.5, 40.3, 112.5, 121.4, 122.8, 124.6, 126.1, 127.1, 132.2, 133.4, 135.5, 135.8, 136.2, 140.7, 149.9. HRMS (ESI) cal. for C₂₈H₂₅ClNS₂ [M+H] 414.11, found 414.11.

Switch **4** (400 mg, 0.966 mmol) was dissolved in anhydrous THF (40 ml) under a nitrogen atmosphere and *n*-BuLi (1.6 M in hexane, 1.105 mmol) was added dropwise. The solution was stirred at room temperature for 1 h and then B(*n*-OBu)₃ (1.111 mmol) was added. The reddish

solution was stirred for an additional 1 h at room temperature and then used directly in a Suzuki cross-coupling reaction.

In parallel, a mixture of 4-bromopyridine hydrochloride (206.7 mg, 1.063 mmol) $\text{Pd}(\text{PPh}_3)_4$ (223.3 mg, 0.193 mmol), aqueous Na_2CO_3 (2 M, 10 ml) and ethyleneglycol (0.3 ml) in THF (20 ml) was heated to 70 °C. The crude boronic ester, prepared as described above, was added and the mixture was heated at reflux overnight. After cooling, the mixture was diluted with diethyl ether and H_2O . The organic layer was dried over Na_2SO_4 , concentrated *in vacuo* and subjected to column chromatography (SiO_2 , 5% ethyl acetate in DCM) to give a solid **1** (92.6 mg, 21%). ^1H NMR (400 MHz, CD_2Cl_2) δ 1.95 (s, 3H), 2.03 (s, 3H), 2.05–2.12 (m, 2H), 2.82 (t, J = 8.0 Hz, 4H), 2.93 (s, 6H), 6.65 (d, 2H), 6.84 (s, 1H), 7.26 (s, 1H), 7.32 (dd, J = 8.0 Hz, 4H), 8.47 (bs, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 14.0, 14.5, 23.0, 38.3, 38.4, 40.2, 112.4, 121.5, 122.7, 126.0, 127.5, 132.2, 133.5, 136.0, 136.2, 137.9, 138.5, 140.6, 149.8. HRMS (ESI) cal. for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]$ 457.18, found 457.18. Elemental analysis: cal.: C 73.6%, H 6.2%, N: 6.1% S: 14.0%; found: C 73.3%, H 6.2%, N: 6.1%, S: 13.9%.



1,2-Bis(2'-methyl-5'-phenylthien-3'-yl)cyclopentene **2** was synthesized according to previously reported procedures.⁷

UV/Vis absorption spectra of ZnTPP and of **1** in the open and closed states

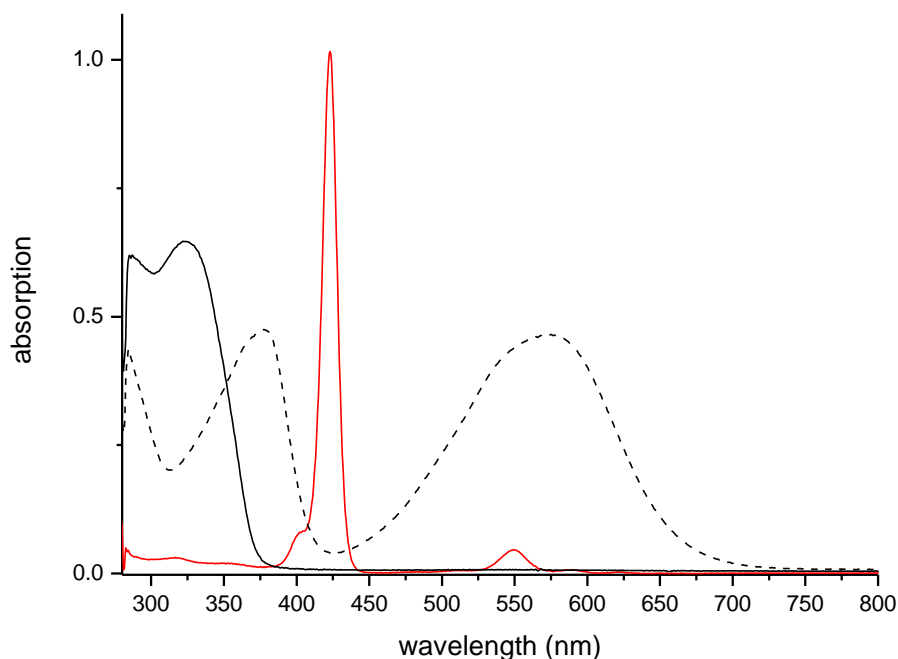


Figure S1. UV/vis absorption spectra of the open form of **1** (20 μM) (black solid line) and of **1** at the PSS_{312 nm} (black dash line), and of ZnTPP (2 μM) (red solid line) at room temperature in toluene.

Determination of association constants

The association constants of the open and closed forms of **1** to ZnTPP were determined by titration monitored by UV/vis absorption spectroscopy. 4 μl of a stock solution containing a mixture of 2 mM of the open or closed form of **1** and 2 μM ZnTPP in toluene (to hold the concentration of ZnTPP constant during the titration), was added into a solution of ZnTPP (2 μM , 2 ml) repeatedly. A red shift of the Soret band of ZnTPP was observed with an isosbestic point at 426 nm with both of the open and closed form of **1**. For the closed form, the overlap in absorption with ZnTPP was subtracted using a reference titration with equal concentrations of the closed form of **1** without ZnTPP. The binding constants were obtained by fitting assuming 1:1 complexation:⁸

$$A = A_0 - \frac{1}{2} \varepsilon_r \left[H_{tot} + G_{tot} + \frac{1}{k_a} - \sqrt{\left(H_{tot} + G_{tot} + \frac{1}{k_a} \right)^2 - 4 H_{tot} G_{tot}} \right]$$

Where A is the absorbance at the 427 nm, A_0 is the absorbance without **1** present, ϵ_r is the relative molar absorptivity, H_{tot} is the total concentration of ZnTPP and G_{tot} is the total concentration of **1**.

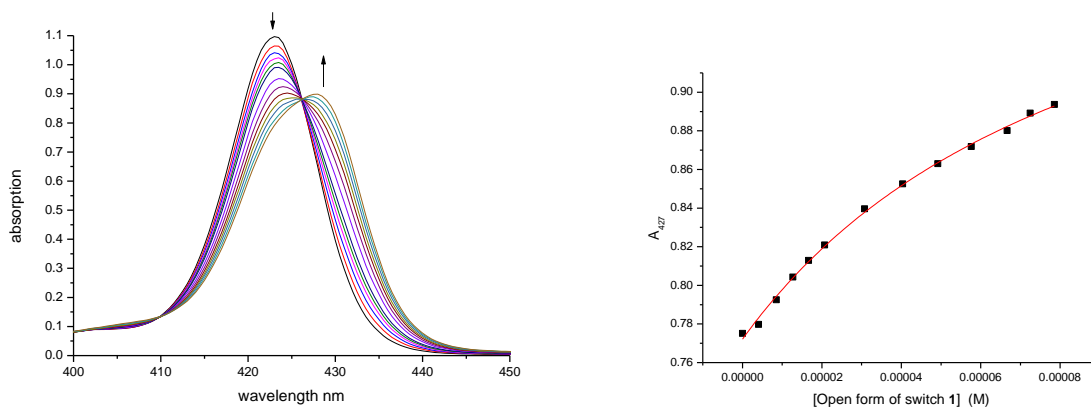


Figure S2. Changes in the UV/vis absorption of ZnTPP upon titration with the open form of **1** in toluene (left) and the absorbance change at 427 nm (right).

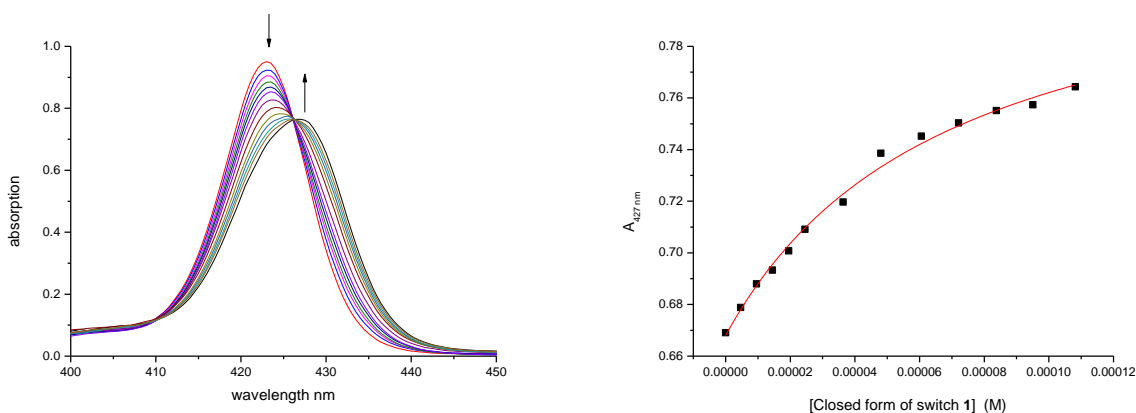


Figure S3. Changes in the UV/vis absorption of ZnTPP upon titration with the closed form of **1** (PSS_{312nm}) in toluene (left, the overlapping absorption with ZnTPP was subtracted using a reference titration with equal concentrations of the closed form of **1** without ZnTPP) and the absorbance change at 427 nm (right).

NIR emission spectra of $^1\text{O}_2$ generated by ZnTPP and ZnTPP mixed with 1 in the open form

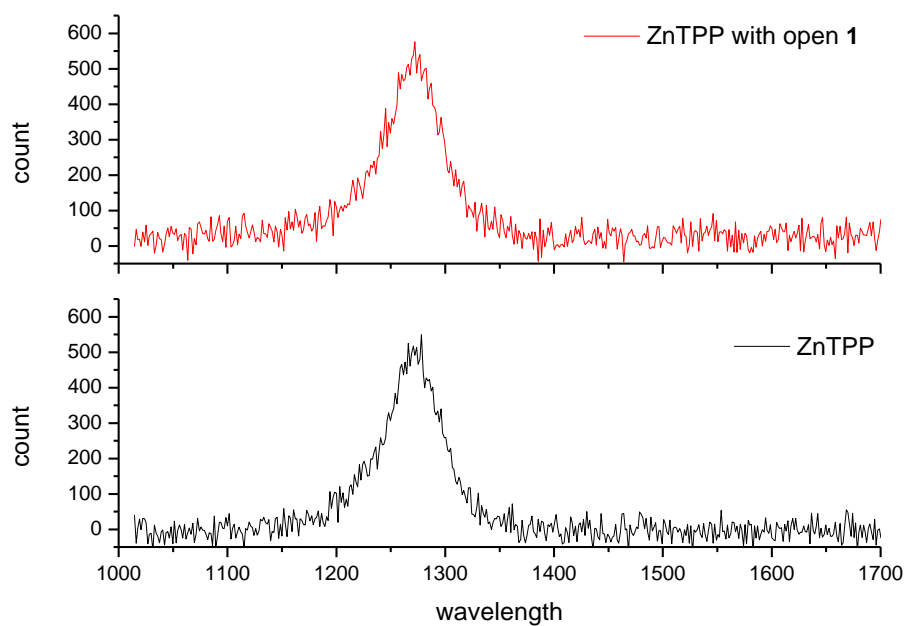


Figure S4. NIR emission of $^1\text{O}_2$ generated by ZnTPP (6 μM) (black) and ZnTPP (6 μM) in the presence of the open form of 1 (30 μM) (red).

NIR emission spectra of $^1\text{O}_2$ generated by ZnTPP mixed with 2

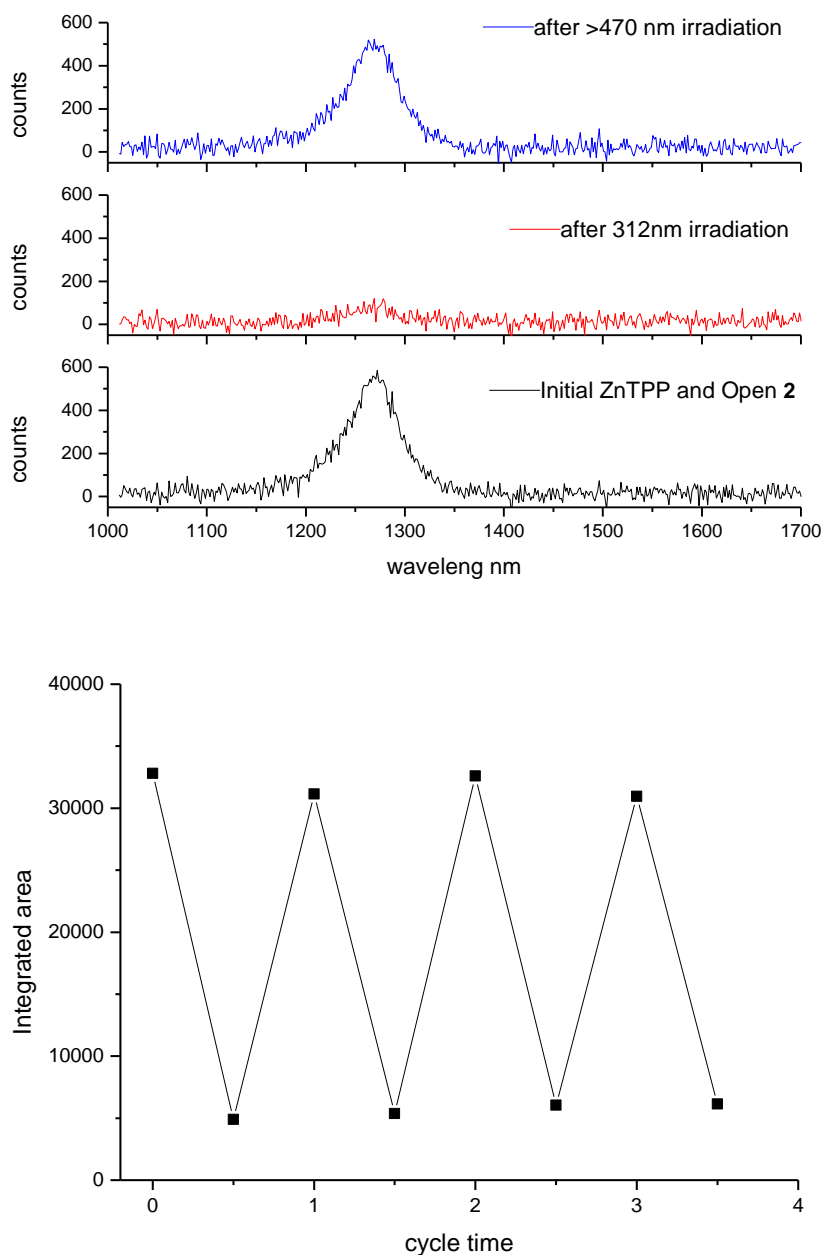


Figure S5. NIR emission of $^1\text{O}_2$ generated by ZnTPP (6 μM) in the presence of 2 (30 μM) and in air equilibrated toluene; excitation at 405 nm (4 mW). $^1\text{O}_2$ generation was observed (upper, black) with the open form of 2 present, but not in the presence of the closed form of 2 (upper, red). $^1\text{O}_2$ generation was recovered by irradiation at >470 nm (upper, blue). The reversibility was monitored by integration of the area of the emission band at 1270 nm over four cycles (bottom).

Determination of singlet oxygen quenching constants

The quenching constants were calculated using the Stern–Volmer equations.

$$\frac{I_0}{I} = 1 + k_D \tau_0 [Q]$$

$$\frac{I_0}{I} = 1 + k_D + k_S \tau_0 Q + k_D k_S \tau_0^2 Q^2$$

Where I_0 is the intensity of the emission at 1270 nm without switches present, I is the intensity of the emission at 1270 nm at different concentration of the closed form of **1** or **2**, k_D is dynamic quench constant, k_S is static quenching constant, τ_0 is the lifetime of singlet oxygen in toluene, and Q is the concentration of closed form of **1** or **2**. The lifetime of $^1\text{O}_2$ generated in a ZnTPP toluene solution is taken as 30.3 μs .⁹

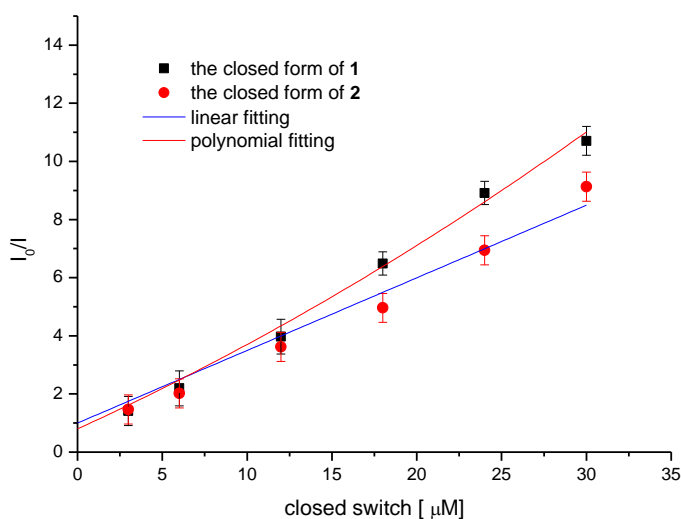


Figure S6 Stern–Volmer plot for quenching of the triplet state of ZnTPP by $^1\text{O}_2$ and by the closed form of **1** (black) and of **2** (red).

$^1\text{O}_2$ generation by a mixture of ZnTPP and 1 in other solvents

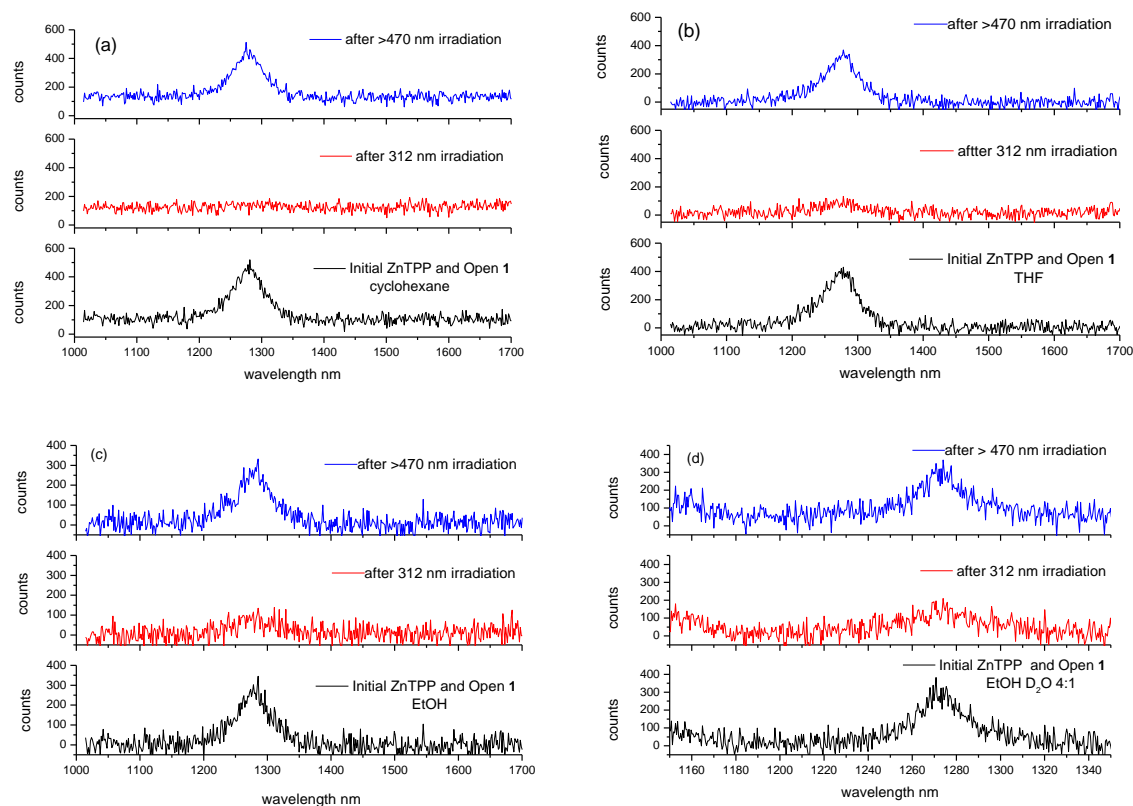


Figure S7. Switching on and off of $^1\text{O}_2$ generation by ZnTPP (6 μM) using 1 (30 μM) in (a) cyclohexane, (b) tetrahydrofuran, and (c) ethanol and (d) ethanol mixed with D_2O (4:1).

$^1\text{O}_2$ generation by a mixture of H_2TPP and 1

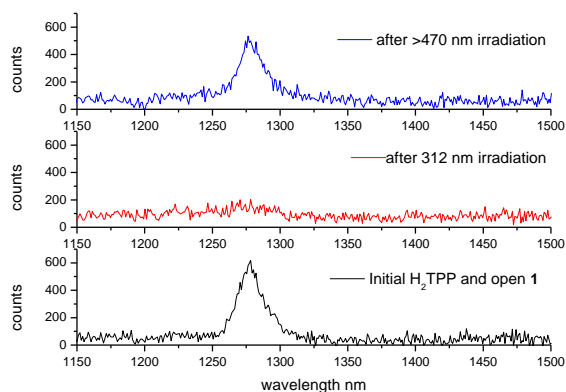


Figure S8. Switching on and off of $^1\text{O}_2$ generation by H_2TPP (6 μM) using 1 (30 μM) in toluene.

Transient absorption of ZnTPP

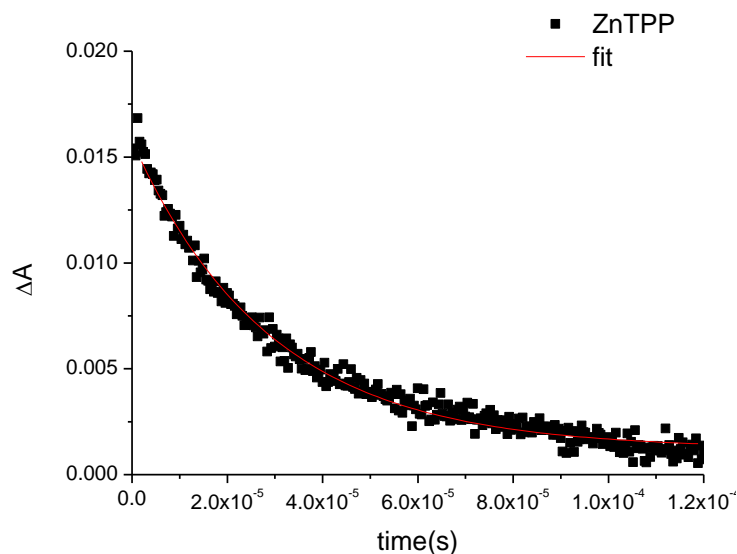


Figure S9. Transient absorption decay trace at 460 nm of ZnTPP (40 μM) in toluene upon excitation at 355 nm. Fitting of the decay of with a single exponential function yields a value of 30 μs .

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